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Proso Millet (*Panicum miliaceum* L.) a Sustainable Raw Material for the Malting and Brewing Process: A Review

On going research further substantiate that consumption of whole grains and grain-based products is associated with health benefits and risk reduction of chronic diseases. Epidemiological studies on these cereals continue to generate an increasing interest on cereal products. This attention also concerns the beverage industry and in the present study, more specifically, malt and beer production, connected with an expansion of the market for gluten free beers. A declaration as an ecological and natural produced good is willingly carried out by the producers. Malted cereals will be appropriate for that kind of declaration because, for brewing purposes, suited malt will offer a good fermented product derived from a simple and well-known technology. More importantly, easy availability is an essential advantage.

Proso millet (*Panicum miliaceum* L.) has a high potential as an alternative food ingredient especially in regions, where the appropriate growing conditions for cereals like wheat, barley, among others, are not met. This paper reviews publications and technical literature on *P. miliaceum.* By doing so, it provides an overview of the cereal composition and, if found, of its structures' behaviour when used for malt, wort and beer production. Many of the verified publications deal with the study of the use of proso millet for foodstuffs. Nevertheless, the compiled data show a good correlation to those cereals that are well known to be good raw brewing material and are therefore used for malting and brewing purposes.

Descriptors: proso millet, alternative cereal, gluten-free, malting, brewing

1 Introduction

Proso millet (*Panicum miliaceum* L.) is one of the oldest crops known to mankind. It was cultivated in the Neolithic period (8000 B.C.–2000 B.C.) in China [1]. It is reported, that the Chinese farmers cultivated waxy and regular species of proso millet during the Second Chinese Dynasty (1600 B.C.–1300 B.C.) [2]. Additionally, findings in central and eastern regions of Europe suggest the cultivation of proso millet in these areas in the age of the Band Ceramic (~ 5000 B.C.) [3]. Until early 20th century, proso millet had almost vanished as field crop in western Europe [4]. This decrease in importance of proso millet [5] was caused by the introduction of potatoes. However, nowadays, proso millet plays an important role in northwest China, Kazakhstan, as well as Eastern Europe, USA, Australia and in the central and southern states of India. The cultivation of millets slightly increased from 29 million tons in the 1980s up to 33.6 to 37.3 million tons in 2001 to 2005. As shown in Table 1 proso millet is ranked as the third most important millet, after pearl millet (*Pennisetum glaucum)* and foxtail millet (*Setaria italica*) [6]. Despite its importance, for thousands of years, this grain was practically not considered for its malting and brewing relevance. Furtheremore, in literature, barely is specified as traditional malt and brewing cereal.

2 Phytology, classification and cultivation

Proso millet is also known as common millet, hog millet, broom corn, yellow hog, hershey, and white millet [7]. It is an annual cereal producing bright green leaves and small seeds [8, 9]. The proso millet plant is considered a short-day plant, which grows 30 to 100 cm tall with few tillers and an adventitious root system. Proso millet is considered a self-pollinating crop, but natural cross-pollination may exceed 10 % [10]. The seeds are generally oval in shape and about 3 mm long and 2 mm wide and normally smaller than pearl millet (*Pennisetum glaucum)* [10]. Herein the proso millet kernel differs radically from the conventional cereals used for malting. The smaller grains raise less problems regarding transport, but more the slotted germination and kilning floors. Beneficial is the unique size in terms of separation from other cereals, a very important property concerning gluten free

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Tables and figures see Appendix

goods, it is also very easy to handle. However, extensive tests at the Lehrstuhl für Technologie der Brauerei I showed that traditional malting equipment definitely cope with this material. Floor malting was suitable, though the usual layer thickness of 10 cm had to be replaced by a 5 cm one at the stage of strongest growth [11]. The drum germination equipment could only be loaded to three-quarter, so that the air supply area was just covered, but the layer thickness was also significantly reduced.

Proso millet is well adapted to diverse soil and climatic conditions. Being a short-season crop (60–75 days) with a low water consumption, it grows further north (up to 54° N latitude) than the other millets and also adapts well to plateau conditions and high elevations [12]. Proso millet can be cultivated in altitudes up to 3500 m [7]. The annual average of precipitation should be less than 600 mm and the average daytime temperature during vegetation should be above 17 ºC [13, 14]. Furthermore, proso millet has a couple of advantages as it only requires small amounts of nitrogen fertiliser, few problems in crop rotation appear, and above all, it is quiet resistant to plant diseases [15]. Proso millet is definitely a cereal that must be considered (for agriculture or cultivation), e.g. when precipitation in Central Europe should decrease and plants with low water requirements are needed.

Proso millet belongs to the order of *Poales*, to the family of *Gramineae*, to the subfamily of *Panicoideae* and therein to the genus of *Paniceae*, which includes 80 genera. Proso millet is classified in five subspecies depending on the type of panicle (*patetissimum*, *effusum*, *contractum*, *ovatum* and *compactum)* [16]. Within these subspecies, proso millet is divided into varieties, whose distinctive characteristics are grain colour, husk type and the appearance of anthocyane dye in the peduncle-spikes and husks [17]. As shown in figure 1.1 and figure 1.2 proso millet varieties can differ in maturation time, seed size and colour; found in creamy white, yellow, orange, red, black, or brown [9, 10].

3 Structural attributes

As a member of the *Poales* order, proso millet is a monocotyledonic plant, whose identifying characteristic is a single seed leaf [18]. The husks of proso millet have a smooth, even surface [19] and the basic kernel structure is similar to other millets. The principal anatomic components are the pericarp, seed coat (or testa), aleurone layer, germ (or embryo) and the endosperm. The thin pericarp is loosely attached to the endosperm. This "shell" suits very well as filter layer during lautering with a lauter tun. The authors report that so far no other malt has had a quicker lautering performance as proso millet malt. [20] In these so called utricle-type kernels, the pericarp easily breaks away; the remaining seed-coat protects the inner endosperm. The testa simply consists of one layer; thickness is between 0.2–0.4 μm. The aleurone layer surrounds entirely the endosperm and germ. The aleuron-cells, with protein bodies and distinctive spherosomes, are 25–50 μm in length [21]. In comparison to other grains, proso millet has a small sized embryo and hence the endosperm to germ ratio constitutes between 12 : 1 and 11 : 1 [21, 22]. The scutellum consists of irregularly shaped cells and appears in the form of two wing-like expansions [21]. *Lorenz* described angular starch granules in the streaky endosperm and spherical granules in the floury area [19]. *Krishna Kumari* and *Thayumanavan* found a bimodal distribution of the starch granules in shape and size [23]. They observed small spherical, large polygonal and rarely large spherical granules. Overall, the size of the starch granules ranged from 1.3 to 13.5 μm [19, 23, 24] and the mean diameters vary from approximately 4 to 5 μm [24]. Altogether, the starch grains have a smaller diameter than barley. This is a possible explanation for the gelatinization of proso millet at higher temperatures (60–77 °C [25]) compared to barley (60–69 °C [26]). Smaller starch grains are gelatinised at higher temperatures than larger ones, which in turn could be caused by the varying mineral content in the different size starch grains [27]. Scanning Electron Microscopy (SEM) reveals that many large granules show indentations on their surface; this is due to the dense packaging of the endosperm. Lorenz as well as Krishna Kumari and Thayumanavan determined that small protein bodies are attached on starch granules [19, 23]. The protein bodies are concentrated in the peripheral cells of the endosperm, becoming more scattered and less frequent towards the inside. *Jones et al.* reported similar results [27] regarding the protein composition of proso millet. They observed that protein in proso millet consists mainly of globular bodies with a diameter up to 2.5 µm. In the outer endosperm cells some of the globular proteins have been embedded in an amorphous matrix protein, whereas in the inner endosperm only little of matrix protein could be found. However, the protein bodies determined were mainly prolamines.

4 Chemical composition of the proso millet kernel

4.1 Carbohydrates

Proso millet consists of approximately 69.8 % carbohydrates, thus qualifying as a carbohydrate-rich food [28]. The carbohydrates of proso millet are composed of starch, soluble sugars, pentosans, cellulose and hemicellulose [21]. Basically, proso millet is similar to barley, the anhydrous part of carbohydrates, however, is at an average of 77.2 %. This is a difference, which is clearly defined in the yield of the later wort production [30, 31].

4.1.1 Starch

Starch is the most abundant carbohydrate in proso millet with a percentage of 52.1–68.2 % of the whole carbohydrates present [28, 29, 30, 31]. Starch is found as granules in the endosperm; it is composed of the two polymers amylopectin and amylose. Each amylopectin molecule contains up to two million glucose residues in a compact structure [32]. These are aligned circularly in the starch granule. With an increased radius the number of branches required (filling up the space) also arises and consequently concentric regions of alternating amorphous and crystalline structure are formed (see Figure 2.1). Figure 2.2 shows the layout of amylopectin in the starch granule.

Some properties of the structural organization of starch granules are still being discussed. Although starch granules are complex macromolecules, it is widely accepted that the amylopectin polymer is predominantly responsible for granule crystallinity

[33]. Common proso millet ranges from approximately 67.2 to 73.7 %, however, for the waxy types the values increase significantly, ranging from 99 to 100 % [21, 31]. An apparent amylose percentage of the total starch content from 27.2 up to 32.6 % has been determined [24, 31, 34], but in addition values of 0 to 6 % amylose have also been reported [30, 34]. Overall it can be concluded, that the discrepancies in the starch content values as well as the ratio of amylose to amylopectin may be caused by the varied extraction methods but, more significantly, they originate from the different varieties and growth conditions. Furthermore differences in gelatinization temperatures may be explained by the different starch properties. Little is reported on the functional characteristics of proso millet starch. *Tomita et al.* appointed a gelatinization temperature between 67–74 ºC [34], whereas *Yanez* and *Walker* determined the temperature between 76 to 77 ºC (by Kofler Hot Stage) [31]. In contrast to these results, Lorenz and *Hinze* measured gelatinization temperatures between 60 to 64 ºC [35]. However, own screenings of different European varieties reported values between 60–77 °C [25]. Gelatinization temperatures reflect the degree of orderly arrangement of the molecules in the starch granule. A higher gelatinization temperature indicates a higher degree of association [35]. Krishna Kumari and Thayumanavan determined a positive correlation between the amylose content and the gelatinization temperature of approximately 76 ºC [23]. To obtain the degree of disintegration of gelatinized granules, starch is cooked at 95 ºC. The decrease of starch paste viscosity relative to peak viscosity gives an indication how the starch granules are degraded [36]. Proso millet showed the highest value in comparison to other millets [23]. The viscosity of cooked starch agglutinates by cooling down to 50 ºC generally reflects the degree of retrogradation of amylose [36]. Thus, a high viscosity indicates a high degree of retrogradation of amylose and the formation of resistant starch. In comparison to other millets, the value for the aqueous proso starch suspension (with an average starch content of 10 %) is reported to be 850 Brabender units, which is lowest of all. Due to the content of amylase (which is lowest in proso millet), a positive correlation of the cold paste viscosity and the amylose content can be seen [23]. Studies on different rice starch suspensions (rice flour content 10 %) showed similar values of cold paste viscosity for different rice varieties [37]. Studies by Lorenz and Hinze showed that the cold paste viscosity of proso millet (except for one variety) obtained on cooling to 35 ºC and holding the paste for 60 min, was higher than that of wheat [35]. The swelling power of proso millet measured at 60 ºC and 70 ºC demonstrated a higher resistance compared to those of wheat and rye [35]. Because of bonding forces within the starch granule the manner of swelling results in a highly associated starch with an extensive and strongly bonded micellar structure, which is relatively resistant towards swelling [38]. The size of the starch granules and the content of amylose also play an important role referring to the swelling power. The higher the amylose content, the lower the swelling power and the slighter the gel strength for the same starch concentration. This is due to the loosely extended helical chains, which also cause the high viscosity of water-soluble starch [39]. To a certain extent a smaller swelling power due to a high amylose content can be counteracted by a larger granule size [40, 41]. Hence starch granules of proso millet have high amylose content and a strongly bonded micellar structure.

All proso millet varieties examined at the Lehrstuhl für Technologie der Brauerei I had gelatinization temperatures over 67 °C and therefore had to be mashed separately. A kind of adjunct brewing, where one mash is mashed-in above gelatinization temperature, in order to gelatinize the mash. The other mash is mashed-in at a temperature that reaches 50 °C in compound with the first mash, so that important amylolytic enzymes, such as the amyloglucosidase, can attack the already gelatinized starch. [47]

4.1.2 Resistant starch

Resistant starch (RS) is defined as the sum of starch and degradation products of starch not absorbed in the small intestine of healthy individuals [42]. This includes unfermented faecal starch, as well as the fraction that is fermented in the large intestine. Three main types of resistant starch have been identified:

i) physically enclosed starch (type 1),

ii) ungelatinized granules (type 2) and

iii) retrograded amylose (type 3) [43].

The occurrence of RS in foods may have a significant health implication as they can act in a similar way to fibre [44]. RS in proso millet is of 0.4 % w/w dry basis, with an absolute amylose content of 17.2 % (dry matter). This is relatively high, when compared to rice, which has 0.2 % w/w dry basis [45]. The alterations of the native starch by autoclaving and cooling to obtain a certain degree of retrogradation showed an increase of the RS content in proso millet up to 8.5 % w/w dry basis. RS in native and treated starch of millet types were positively correlated with the total amylose content [45].

Experiments with rats on the digestibility of native RS of millets and the rice-variety *Oryza sativa* resulted in the consumption of approximately 50 % of the fed proso-RS. The value of proso millet was significantly higher compared to other millets but still lower than the one of rice variety *Oryza sativa* [45]. Furthermore a significant decrease in digestibility was observed when feeding the rats with treated RS (39.9 % for proso millet). However, proso millet had the highest benefit of all the millets assayed. Compared to a rice diet, a reduction in blood glucose level, serum cholesterol level and serum triglyceride level in rats fed with native starch as well as treated proso millet starch was perceived [45]. Although proso millet starch ranks after some variety of millet starches, it can be considered as a hypoglycaemic and hypolipidemic agent similar to rice starch (*Oryza sativa*). Moreover the hypoglycaemic and hypolipidemic attributes can clearly be increased by using suitable processing parameters.

In addition to its nutritional physiology the resistant starch can contribute to the viscosity of wort. Since the analysed proso millet varieties did not show a viscosity higher than 1.5 mPa × s neither in the congress wort, in the Eyben wort nor in the wort after a perfectly adjusted mashing process for proso millet [46], this fraction can be so far neglected with respect to the technical process [47].

4.1.3 Dietary Fibre

The edible parts of plants or analogous carbohydrates that are resistant to digestion and absorption in the human small intestine with complete or partial fermentation in the large intestine are considered as the dietary fibre (DF) [48]. DF includes polysaccharides, oligosaccharides, lignin and associated plant substances. Dietary fibres induce beneficial physiological effects including laxation, blood cholesterol attenuation, and/or blood glucose attenuation [48]. Nevertheless, because dietary fibres bind minerals, these can cause negative effects when the DF intake is fortified in an unbalanced diet [49]. DF contents ranging from 2 % up to 20 % have been reported in different sources [50, 51] *Ferriola* and *Stone* reported DF contents of 8.9–12.5 % in a complete proso millet meal with moisture levels of 2.5–5.6 % (according to the American Association of Cereal Chemists (AACC)) [52].

According to the results of Ferriola and Stone [52], *Geervani* and *Eggum* [51] and *Deloste-Lewis et al*. [50] the DF content in proso millet is much higher than in other common cereals like wheat and rye, 2.9 % and 2.8 %, respectively [53]. Deloste-Lewis et al. observed a loss of DF due to a puffing process [50].

Proso millet contains 0.4 % hemicellulose and 2.7 % cellulose. The hemicellulose is mainly composed of glucose, arabinose, uronic acid and xylose units [21]. As in barley, these substances can amount up to 10 % of the dry matter [11], whereby its composition is very similar to proso millet. Their content, however, is not alike, a fact that can be recognized on the already mentioned low viscosity of proso millet malt worts (see 4.1.2). By means of the fluorometric method, with which β-glucan molecules over 10,000 Dalton are measured [59], no relevant content on viscosity-increasing substances could be proved.

4.1.4 Saccharides

By extracting with 70 % ethanol solution, *Becker* and Lorenz studied the saccharide composition of eight proso millet samples. In their research they could only find monosaccharides traces of glucose, fructose and galactose. Prevailing sucrose with a fraction of 0.5–0.9 % of dry weight, values are comparable to other cereal grains, as reported by [54, 55]. Raffinose as the next abundant sugar occurred with 0.04–0.10 % at only about 1/10 the amounts in mature kernels of wheat, rye and triticale [54, 55]. Myo-inositol (which is not a carbohydrate by definition, as it belongs to the chemical class of cyclitols [56]), was found in minor quantities up to 0.01 %. Neither maltose nor maltotriose have been detected in proso millet [54].

This original content on saccharides will fundamentally be changed during malting process and plays no direct role for wort composition. Due to the unusual amylolytic enzyme ratio, completely different assignements of fermentable saccharides [63] result for wort production compared to barley malt wort.

4.2 Proteins

They are of great technological significance as well as an important part of the biological processes. Thus they have a substantial influence on all process steps during malt and beer production. Additionally, they partly determine yeast nutrition and beer quality parameters like foam, taste and stability.

4.2.1 Storage Proteins

Storage proteins (SP) account for about 50 % of the total protein content in mature cereal grains. They have an important impact on the nutritional quality for humans and livestock, as well as on the functional properties in food processing [57]. SP are mainly generated during seed production and stored to serve as nitrogen source during germination. Storage proteins (which as such are still not clearly defined) usually have no enzymatic activity and generally consist of a number of different polypeptide chains [58]. SP normally occur in an aggregated state within a membrane surrounded vesicle (protein bodies, aleurone grains).

Throughout the years, different protein classification models have been developed. Depending on the grain proteins' solubility, *Osborne* (1907) divided these into four groups:

i) albumins are soluble in distilled water and dilute buffers at neutral pH;

ii) globulins, which are soluble in salt solutions but not in distilled water;

iii) glutelins, soluble in dilute acid or alkali solutions and iv) prolamins are soluble in aqueous alcohols of 70–90 % [59, 60].

Alternatively, *Landry* and *Moreaux* (1970) divided the proteins into five classes:

i) fraction I, albumins and globulins;

ii) fraction II, true prolamin;

iii) fraction III, prolamin like;

iv) fraction IV, glutelin like; and

v) fraction V, true glutelin [61].

4.2.2 Amino Acids composition

The quality of a protein is primarily determined by its essential amino acid composition. Essential amino acids are those which can not be synthesised by the human body as opposed to the non-essential that can be synthesized if the necessary chemical components are available in the human system [62]. The protein content (6 to 16 %) in proso millet grain caryopsis is comparable with maize. The protein content depends on variety, water content, soil nutrients, as well as the conditions during grain formation [27, 28, 63, 64, 65, 66, 67, 68, 69]. Table 2 shows the amino acid composition in proso millet. The values in table 2 are comparable to those shown in a modified table by *Serna-Saldivar* and *Rooney* [21].

Low-molecular nitrogen components, in particular amino acids in wort, influence the fermentation and the development of secondary metabolites and flavour compounds. Concentration and composition of the amino acids are therefore important for the flavour profile of beer; besides, the reactivity with reduced sugars (Maillard reaction), in particular with the kilning of malt and during mashing and/or wort boiling come about. These reaction products affect redox potentials, colour and flavour of the beer. [59] 169

4.2.3 Inhibitors

Enzyme inhibition is the negative influence of an enzymatic reaction by a restrictor, called inhibitor. The speed of the reaction is lowered or blocked. The inhibitors can bind to different substances involved in the reaction, e.g. to the enzyme or the substrate. As different fractions of the grain come into contact during milling, such inhibitors can possibly block the malt enzymes (e.g. the monomeric α-amylase-inhibitor-1 (BMAI-1) = Hor v1 [78] in the case of barley). Actually these inhibitors are necessary for the biochemical adjustment of starch degradation during germination.

In proso millet protease inhibitors are distributed in seeds and leaves., Such components have been identified in most plants [70]. These inhibitors are, usually, heat labile proteins that can bind to the active site of vertebrate digestive enzymes with very high affinity.

The presence of protease inhibitors in seeds is not completely understood but the following functions are known:

i) storage - in some cereals trypsin inhibitors can contribute to 5–10 % of water soluble proteins,

ii) control of endogenous enzymes – some authors believe inhibitors control activity of proteolytic enzymes and

iii) protection. Moreover, protease inhibitors might inhibit proteolytic digestive enzymes of invading insects or secretive protease of micro-organism [59].

Ravindran, using *Kakade et al.* [71] methods, researched trypsin and chymotrypsin inhibitory activitiy [69]. Activity was measured as trypsin inhibitory units (TIU) or chymotrypsin inhibitory units (CIU) and expressed as numbers of trypsin units (TU) or chymotrypsin units (CU) inhibited per gram dry weight. TUs or CUs are defined as the increase of 0.01 absorbance units at 280 or 275 nm, respectively. Compared to chymotrypsin inhibitory activity (62 ± 6.6 CIU), higher inhibitory activity values (732 ± 11.7 TIU) were recorded for trypsin, as opposed to *Gudiseva Chandrasekher et al.* who had no detectable protease inhibitory activity during the screening of 13 varieties of proso millet [72].

In addition to protease inhibitors, *Nagaraj* and *Pattabiraman* purified a type of α-amylase inhibitor, specific for human pancreatic amylase, from proso millet seeds [73]. This inhibitor was more effective by two orders of magnitude in its action on human pancreatic amylase than on human salivary amylase. This attribute makes the inhibitor suitable for application in differentiating salivary and pancreatic amylases in the serum for diagnostic purposes. Chemically modified studies revealed that amino and guanido groups are essential for the action of the inhibitor. The calculated molecular weight based on the mobility during SDS-PAGE was 14 kDa, which correlates to the value obtained when using gel chromatography 13 kDa.

Pepsin was found to rapidly inactivate the inhibitor and complete abolition of amylase inhibitory activity was observed within 20–30 min. Trypsin and chymotrypsin were relatively slow in this respect. It was only after 8 h of interaction with these enzymes that proso inhibitor completely lost its activity. Pronase was found to inactivate the inhibitor in 2 h. Other studies showed the effect of the proso millet α-amylase inhibitor against human and bovine enzymes and observed weak activities against guinea pig, rat, and dog amylases and even no activity against cat, rabbit, chicken, equine and porcine enzymes [74].

Proso millet inhibitors, like other cereal inhibitors, may be of high nutritional relevance in terms of digestibility since studies show that heating, processing (e.g. malting) of human enzymes like pepsin decrease its biological action to an insignificant level [21, 73, 75]. However the inhibitor will find application in differentiating salivary and pancreatic amylases in the serum for diagnostic purposes.

4.3 Lipids

Naturally, lipids in cereal grains are relatively minor constituents [21]. Barley contains up to 2 % fat in the dry matter. During malting the fat is partially consumed and, in doing so, it conduces to aerobic metabolism. The majority remains in the spent grains. Nevertheless, the fatty acids are important for the yeast nutrition. On the other hand they have a negative influence on flavour stability. Likewise foam-negative effects were observed. [85] By using different extraction methods, total lipid contents of 4.1 to 9.0 % (dry weight based) have been found in whole grains of different proso millet varieties. From the total content, 3.8 to 5.6 % were free lipids (FL), 0.6 to 2.5 % bound lipids (BL) and 0.9 % were assigned as structural lipids [68, 76, 77]. However, information on the lipid composition plays an important role to assess the storage stability as well as nutritional properties [77].

As most of the lipids are located in the scutellum, lipid contents are significantly reduced when kernels are decorticated and/or degermed [21]. *Sridhar* and *Lakshminarayana* divided the lipids into three major classes;

i) nonpolar lipids (NL),

ii) glycolipids (GL) and

iii) phospholipids (PL) [76].

The NL constitute the major portion of total lipids ranging from 80 to 83 %, whereas the GL and PL contents varied at 6–14 % and 5–14 %, respectively. NL, GL and PL are further divided into subclasses. The constituents of the different lipid subclasses and their fatty acid composition are shown in table 5 and table 6.

As shown in table 5 and table 6 the major components of the lipids are triacylglycerols, whose esterified fatty acids are mainly linoleic acids (18 : 2] followed by oleic acid. These results correlate with the observations done by *Gabrovská et al.* [68] and Lorenz and *Hwang* [77]. Regarding the nutritional value, proso millet lipid composition can be considered favourable, because linoleic acid is essential for humans as a precursor of arachidonic acid. Arachidonic acids, essential for the synthesis of prostaglandins, such as, thromboxan and prostacyclin have a preventive effect against cardio- and angiopathy [78]. Unfortunately the high fraction of unsaturated fatty acids causes a high sensitivity to lipid oxidation during storage, especially if the grain has been milled. Nevertheless, *Bookwalter et al.* demonstrated the inactivation of lipase by a 97 ºC heat-treatment to minimize fat hydrolysis [79].

4.4 Minerals

In barley the total quantity of minerals amounts 2.5-3.5 % of dry matter. Depending on the conditions of fertilization, climate and soil the individual percentage can vary. These mineral nutrients are of great importance for germination and, in addition, for the later fermentation.

A good deal of information in literature about the mineral content in proso millet originates from the field of the science of nutritional units. Among functional food components minerals play an essential role. Deficiencies in essential minerals are seen as a major nutritional problem in the modern world. Proso millet is an important source of minerals. The pericarp, aleurone layer and germ are rich sources of ash [21]. Table 7 shows mineral contents measured in proso millet as well as the recommended daily intake.

Proso millet is a poor source of calcium; potassium and phosphorus are the minerals found in greatest quantities. However, as bioavailability is influenced by many parameters, the value does not state much about the nutritional value of minerals. One important bioavailability parameter is phytic acid, whose average amount found in proso millet is 0.61 g/100 g (dry weight basis), comparable to that found in other cereals [54, 69]. As the principal storage form of phosphorus (67.3 % of the phosphorus in proso millet) in grains, it highly affects the bioavailability of this mineral as non-ruminant animals lack the digestive enzyme phytase, which is required to separate phosphorus from the phytate molecule [69, 80]. Although phytic acid is a strong inhibitor of iron absorption in both infants and adults, its influence on zinc absorption in infants seems to be modest and perhaps most important in children recovering from infection. The influence of phytic acid on calcium and magnesium absorption seem of minor importance, even an older study reports that only 43 % of calcium in finger millets was retained by rats due to the adverse effect of high phytate content [81, 82]. The impact of different parameters related to bioavailability can be influenced by processing proso millet. Processing can have a positive impact as a result of separation, partitioning of minerals (enrichment), the destruction of inhibitors or the beneficial complex formation between food components and metal ions, thereby enhancing their availability. However, the impact can also be negative by deactivating enzymes that degrade inhibitors or by generating insoluble metal compounds (e.g. oxidation, precipitation) [83].

The Lehrstuhl für Technologie der Brauerei I produced many beers with proso millet malt. Average mineral contents were identified here. This shows that yeasts are primarily responsible for the resulting mineral content. No striking fermentation behaviour could be observed when common top-fermentating yeasts were used [94].

4.5 Vitamins

Also the vitamin contents of the analysed proso millet varieties could only be found in literature of nutrition science. Vitamins for the brewing process are of superior importance for the living process of germination, yeast growth and fermentation [85]. Barley and its malt are rich in vitamins, which are located in the living tissue of the seedling and the aleurone layer. Vitamins are important organic compounds, which can not, or not in sufficient quantity, be synthesised by the human body. Hence, it is necessary to provide the human organism with adequate amounts of vitamins during a supplemented diet. Vitamins are mainly divided into two groups: i) fat-soluble vitamins include vitamin A (retinoids), vitamin D (calciferols), vitamin E (tocopherols), vitamin K (naphtochinones) and ii) water-soluble vitamins, in which vitamin B_1 (thiamines), vitamin B_2 (riboflavins), niacin (nicotinic acid), Vitamin B_6 (pyridoxines), folic acid, pantothenic acid, biotin, vitamin B_{12} (cyanocobalamines) and vitamin C (ascorbic acid) are found [84].

Proso millet is a good source of B vitamins except for vitamin $B_{12.}$ The B vitamins are concentrated in the aleurone layer and germ. Removal of these tissues by decortication reduces the content whereas malting and fermentation increase the amount of B vitamins and their availability [21]. Table 8 shows value ranges of proso millet vitamin contents and their recommended daily intake.

The noticeable problems during fermentation of proso millet malt worts were previously mentioned in chapter 4.4 and can also be applied for the vitamins. In several propagations, which were necessary to actually produce gluten-free yeast, no quality-reducing delays were noticed.

4.6 Phenolic antioxidants

Although phenolic antioxidants are present in barley in small quantities (0.1 to 0.3%), they still influence several beer characteristics, e.g. colour, foam, stability and taste. In human bodies oxidative damage has been attributed to a number of diseases, including cancer, cardiovascular disease, arthritis and aging; antioxidants are widely believed to be important protectors against oxidation [85]. Phenolics are good antioxidants because of their favourable redox potentials and the relative stability of the aryloxy radical [86].

4.6.1 Phenolic Acids

Phenolic acids are hydroxylated derivatives of benzoic and cinnamic acids (Fig. 3). The Following phenolic acids were proven in barley: vanillic acid, which appears in free form as well as in bounded form in the husks, also syringic acid, ferulic acid, p-hydroxy-benzoic acid and the coumaric acid [98]. Further substances, which partially function as germination inhibitors [85], can be proven in bounded form as glykosides and esters. In proso millet, as well as sorghum and other millets, they are primarily located in the outer layers but can also be found in the endosperm [87, 88, 89]. Phenolic acids possess potential health-promoting properties, partly by virtue of their antioxidative action [88]. They mostly appear in bounded form with types of sugars or sterines. Esters of sterine and phenol acids have a cholesterol-lowering effect and are also effective antioxidants. Compounds of ferulic acids and sterines, so called sterylferulate esters, showed distinctive protective effects against LDL-cholesterol [90]. When rats were fed with sorghum and proso millet at 30 %(w/w) of the total diet the HDL-cholesterol level increased without changing the total cholesterol level [91].

Hydroxycinnamic acids are more common than hydroxybenzoic acids and consist of *p*-coumaric, caffeic, ferulic and sinapic acids. Several of these phenolic acids are found in grain products, ferulic acid being the most abundant [88, 92, 93]. Phenolic acids are particularly interesting as they are potentially protective against cancer and heart diseases [92, 93, 94]. The total content of phenolic acids in proso millet whole grain grits were analyzed according to *Mattila et al.* [88] (shown in table 9).

Table 9 shows that the composition of phenolic acids is typical for other grain products containing mainly ferulic acid, *p*-coumaric acids, as well as ferulic acid dehydrodimers.

4.6.2 Tannins

Dietary tannins are often perceived as detrimental, however, *Hagerman et al*. suggested that tannins, or polymeric polyphenolics, may be much more potent antioxidants rather than simple monomeric phenolics [95]. Although many small phenolics are pro-oxidants, tannins had little or no pro-oxidant activity. However, the potential of tannins to diminish nutrient digestibility must be balanced against their potential to serve as biological antioxidants [96].

Because of the complex nature of the mixture of phenols in barley and because of their instability under a range of conditions and in the presence of air, they are difficult to characterize, and methods for their quantification are only partly successful. Therefore phenols with “tannin” ability have been characterized by their ability to form haze or to precipitate with solutions of standard proteins, cinchonine sulphate or soluble polyvinylpyrrolidone. [97]

Using the modified vanillin-HCL method Lorenz determined tannin contents of 24 proso millet varieties with different seed colours [98, 99]. Dark-coloured seeds had higher tannin contents than light-coloured seeds. As dehulling greatly reduced the levels of tannin, it is evident that tannins are mainly inherent in the hulls. Amounts of tannins ranged from 0.05 to 0.18 % catechin equivalent at an average moisture level of 9.2 %. However, these values should be regarded critically, as the vanillin-HCL method is not specific, since it extracts the condensed tannins as well as monomeric flavanols and their oligomers [100]. Investigations on sorghums which do not have a pigmented testa contain non-tannin phenolics that react with the reagents and give some “tannin values” not corresponding with real tannin amounts [101, 102, 103].

Choi et al. determined antioxidant activity of the methanolic extracts and correlated antioxidant activities with the antioxidant contents in the different extracts [104]. The concentrations of total polyphenol and carotenoids in the extracts were measured by spectrophotometric methods and vitamin E analysis was carried out using HPLC. In comparison to red sorghum and black rice, proso millet showed significantly lower antioxidant activities and lower polyphenol contents; however the values are similar to those of white rice, brown rice, mungbean, foxtail millet, barley and adlay. Nevertheless, no correlation was found between antioxidant activities and carotenoids and vitamin E derivatives.

4.7 Enzymes

The hydrolyzing enzymes are an important factor in the beer production process. By definition, beer actually only differs from wine by the fact that the source of fermentable carbohydrates are enzymatic hydrolysed from starch. Thus the amylolytic enzymes catalyze the crucial step of the wort production, in which starch is divided into soluble and fermentable carbohydrate components. Proteolytic enzymes hydrolyze the polymer protein into many different fractions. These fractions have essential influence on yeast nutrition, turbidity inclination in general, taste, foam and their stabilities. Then the cytololytic enzymes, which ensure the process capability of wort and beer by decomposing the cell wall components, such as β-glucan. Literature supplies limited information about the cereals analysed here.

4.7.1 α-amylase

α-amylase hydrolyses starch, glycogen and other 1,4-α-glucans. The cleavage occurs from the inside of these molecules. Amylose is split into oligosaccharides of 6–7 glucose units. Amylopectin is unspecifically cleaved, whereas the 1,6-α-branching point is missed out [105]. In ungerminated, mature proso millet seeds a very low α-amylase activity is measurable. *Parvathy and Sadasivam* germinated proso millet seeds by placing them on a double layer of moistened filter paper in Petri dishes and kept them at 29 ºC in the dark for one to eight days [106]. After a two-day lag period, the activity strongly increased reaching its maximum on day five. Thereafter, within three days, the activity almost decreased to the initial level. *Zarnkow et al.* reported, that compared to barley malt, α-amylase activity in proso millet malt is relatively low [47].

Internal tests showed that temperature and pH-optimum in proso millet malt worts can be determined as 60 °C with pH 5.0 [119].

4.7.2 β-amylase

β-Amylases are exo-hydrolases that release maltose from the non-reducing end of α-1,4-linked poly- and oligoglucans to the first α-1,6-branching point along the substrate molecule it encounters [107]. *Yamasaki* isolated β-amylase from germinating proso millet seeds [108]. The enzyme was homogeneous using SDS-PAGE. Based on its mobility on SDS-PAGE and gel filtration with TSKgel G4000SWXL, the molecular weight of the enzyme was estimated to be 58 kDa revealing that it is composed of one single unit. The enzyme activity significantly increased during germination between day one and four. In accordance with the increasing enzyme activity, germination of the seeds is markedly enhanced. The enzyme hydrolyzed malto-oligosaccharides more readily as their degree of polymerization increased. It was strongest for malto-oligosaccharides larger than 13 glucose residues and very weak for maltotriose (e. g. amylopectin). Soluble starch was hydrolysed three times faster than maltoheptose. Amylose, amylopectin and soluble starch were the most suitable substrates for the enzyme. Starch digestion was accelerated 2.5-fold when β-amylase was added to a reaction mixture containing α-amylase, pullulanase and α-glucosidase. Thus, β-amylase should be a key enzyme in starch degradation during the germination of millet seeds.

β-amylase is stable in a pH range of 3.5–9.0, the optimum pH was found to be 5.5–6.0 which is 0.5–1.0 higher than *Skovron* and Lorenz hypothesised. The optimum temperature was established to be 55 ºC. Preincubation with 5mM of metal ions, Hg^{2+}, Mn^{2+} and Cu^{2+} , at 37 ºC for 30 min, reduced the β-amylase activity by more than 80 % [108]. However, depending where the grain was cultivated – even within the same harvest – different values are recorded. Thus, enzymatic activity is very difficult to assess [109].

Unlike barely malt, observations showed that β-amylase also occurs in considerably lower concentrations in proso millet malt. Thus the plant focuses less on these enzymes while starch decreases during germination. Nevertheless, in own trials temperature and pH-optimum could be determined for the previously isolated proso millet β-amylases (40 °C with pH 5.3) [119].

4.7.3 *α-glucosidase*

During the early stage of seed germination, α-glucosidase plays an important role in terms of seed respiration, additionally its capacity to liberate glucose from starch doubles after 24 hours of germination (soaking). Until there, α-amylase is still in the lag period, with no visible activity [110] Conversely, some authors [111, 112] claim, that α-glucosidase is part of the non-phosphorolytic pathway for the breakdown of starch and plays a role in seed germination by hydrolyzing the oligosaccharides produced by α- and β-amylases. However, *Sun* and Henson reported that barley seed α-glucosidase can initiate the attack of raw starch granules, and that this attack is independent of the presence of α-amylase [113]. Using fractionation and preparative gel electrophoresis, Yamasaki et al. isolated two types of α-glucosidase (I and II) from proso millet seeds [114]. The two enzymes showed identical molecular weights, calculated to be 85kDa on SDS-PAGE and 93kDa on gel filtration. The optimum pHs of the two α-glucosidases were found to be 3.5 and are stable in a pH-range of 3.5–6.0 (I) and 3.5–5.5 (II). The temperature optima of the two α-glucosidases were found to be at 60 °C. The two enzymes hydrolysed maltose and malto-oligosaccharides. α-glucosidase (II) hydrolysed native starch from millets seeds weakly. α-glucosidase (I) showed activity reduction after incubation with Hg^{2+}, Zn^{2+} and Cu^{2+} of 20 % and more, whereas α-glucosidase (II) activity was not inhibited by Zn^{2+} and Cu^{2+}. Yamasaki et al. also reported that the activity doubled after the proso millet seeds had been soaked in water for 24 h [110]. Thus the conformation of the enzyme protein may have changed to show higher enzyme activity than that in intact seeds. The α-glucosidases showed a higher affinity for polysaccharides than for maltose, even at considerably low concentrations compared with maltose. The Michaelis-Menten constant for maltose, K_m value, is lower than those of α-glucosidases from other plants, such as rice seed [115], buckwheat [116], sugar beet [117, 118] and barley [119]. The K_m value for malto-oligosaccharides decreased with an increase in the substrate's molecular weight. The α-glucosidase may preferably hydrolyze oligo-saccharides liberated from starch by α-amylase to glucose without the preceding action of ß-amylase during the germination of millet seeds, although it has been suggested that α-glucosidase needs the preceding action of α- and ß-amylases to play a role during the germination of plants [111, 112].

The internal tests showed that the plant lays its focus on the decrease of the reserve substance starch with this enzyme during germination [47]. Temperature and pH optima for α-glucosidases could be determined in proso millet malt wort at 50 °C with a pH of 5.3 [119].

4.7.4 *Protease*

Little is known about the protease activities in millets in the literature to date. Skovron and Lorenz examined proteases from eight different proso millet cultivars extracted at different pH values [109]. In all cases protease activity was higher in the pH 4.8 extract than in the pH 3.8 one. The protease activity in rice is comparable to the activity in proso millet [120].

4.7.5 *Cellulase and hemicellulase*

Skovron and Lorenz measured cellulase and hemicellulase activity in millet varieties. Only a few varieties showed no hemicellulase activity [109].

β-glucan, available in high concentrations in barley and oats, was practically non-existant in proso millet as soluble cell wall substance. However, in internal tests proso millet presented itself absolutely uncomplicated with respect to process suitability, such as lauterability and filterability [134].

5 Use of Proso Millet in Malting and Brewing Process

5.1 Malting

Malting is a process applied to cereal grains, in which the grains are left to germinate and then are quickly dried before the plant develops. The malting conditions of the grain itself are very specific e.g. respective variety and growing conditions. *Khan et al.* ascertained that differences in water uptake and incidence of imbibition damage in proso millet biotypes were associated with seed coat colour [121]. Varieties that had entirely or partly light-coloured seed coats imbibed rapidly and suffered major imbibition damage. Thus, dark pigmented seed colours show a slower rate of seed germination than light-coloured seeds. White-pigmented seeds took the shortest time to achieve maximum germination (36 h), while black-pigmented took the longest (108 h). The differences in rate of germination were related to the rate of water uptake. The major factor influencing water uptake was most possibly the permeability of the seed coat. Coloured seed coats are heavier and therefore presumably thicker than those of light-coloured seeds. Permeability of dark-coloured [120] seed coats may be reduced by a physical barrier of greater cell numbers, by differences in cell density or by some chemical reaction (phenolic oxidation) unique to coloured seed.

Parvathy Parameswaran and *Sadisvam* made an attempt to study the effect of germination on the protein and carbohydrate profile [122]. They soaked the grains overnight in distilled water at room temperature and spread them evenly on filter paper, which was moistened at regular intervals of 24 hours. The germination was carried out at room temperature for 1 to 8 days in the dark. During the early days of germination, the protein content did not differ much, while gradually increasing in later stages. This was due to the loss of dry matter content during germination. After the first day of germination, changes in the relative amount of the protein fractions could be observed. Albumin and globulin fraction continued to increase, inversely, the prolamin fraction continued to decrease [122]. Slight differences were noticed in the glutelin fraction. As germination proceeded, the extractability of the protein was found to increase. The content of non-polar nitrogen, free amino acids, lysine, tryptophan and methionine grew during germination and reached their maximum on the sixth day of germination after which the values declined. During germination, the most significant amino acid changes were the substantial increase in lysine and tryptophan contents. They propose that the significant rise in lysine during germination can be attributed to de novo synthesis.

As for changes in the carbohydrate profile, they ascertained a decrease in the starch content and an apparent initial increase in the amylose content. These changes might be caused by limited hydrolysis of both components of starch by α-amylase [106]. During germination the low molecular carbohydrates production was drastically enhanced, which can be attributed to the degradation of starch. The lowering in the starch content was not entirely reflected in the total carbohydrate content. This may be due to the partial compensation by simple sugars derived from starch [123].

Zarnkow et al. investigated the influence of the different malting parameters such as vegetation time, degree of steeping and temperature on the quality of proso millet malt [47]. They also observed the malting process with scanning electron microscopy [124]. The optimal quality parameters concerning the use of malt for brewing (extract, apparent attenuation limit, α-amylase activity, and β-amylase activity) were achieved after five days vegetation time, 44 % moisture content during germination and a constant temperature of 22 °C during steeping and germination. Further studies related to different proso millet varieties and their ability to create acceptable malt quality attributes lead to several varied recommendations [125, 126].

5.2 Brewing

Bosa, also called busa or bouza [127], product from the Balkans, Egypt, Sudan and Turkey, is one of the traditional beers produced from proso millet. It is a bread-beer and the methods of manufacture are said to resemble those used by ancient Egyptian brewers [128, 129, 130]. The name is derived from *buze*, the Persian word for millet. Boza can be brewed from various cereals, proso millet being the preferred one. It is a thick pale yellow liquid, with a characteristic acid-alcoholic aroma. The alcohol content is generally less than 1 %vol in contrast boza from Egypt can contain up to 7 %vol. To produce this beer, about ¾ of the proso millet charge is coarsely ground and kneaded with water. Alternatively, the dough is made with a mixture of malted and unmalted millets, with yeast added to make the dough rise. After some time the dough is shaped into loaves, and these are slightly baked. Presumably some of the yeast and millet enzymes survive. The remaining millet is soaked and is exposed to the air allowing it to germinate; alternatively, limited germination in the soil may be arranged. After the malt has been dried, the matted roots are removed by hand, first rubbed to polish them and then sieved to separate the fragments. The green malt may be immediately used or first be sun dried. It is crushed and mixed with broken bread lumps and water. The mixture begins to ferment; sometimes some old boza is added to provide an inoculum of microbes. After time the mixture is roughly filtered to remove the coarse solids [97].

Alternatively, *Zarnkow et al.* established a mashing method to produced good quality wort as a basis for gluten free beer [46, 131]. From their research, it was concluded that the usual infusion mashing process applied for barley malt cannot be used for proso millet malt. This is because the gelatinization temperature of proso millet malt is relatively high compared to the gelatinization temperature of barley malt. Moreover enzymatic activities are relatively low and their maxima are reached before gelatinization takes place. Therefore, to make starch more susceptible for enzymatic attack, a partial heating of the mash over gelatinization temperature is recommended. The heated mash blends with the remaining mash in a proportion that the resulting temperature is the lowest one of the temperatures known to be optimal for enzymatic activities. The entire mash will then be heated to the next temperature optimum for specific enzyme activity (infusion mashing). Finally, it is also recommended to adjust the pH value of the mash to the enzyme specific optima at the different temperature steps. Figure 4 shows this recommended mashing programme, which resembles to the mashing of unmalted adjuncts.

Further attempts were focused on wort cooking and the processing of DMS and its precursor DMS-P. Since proso millet basically brings in a somewhat higher potential, boiling times had to be kept under atmospheric conditions over 90 minutes. Further, the finished wort had to be immediately cooled down to a temperature below 80 °C, in order to avoid further splitting of DMS-P into DMS. This wort was fermented with different yeast strains, whereby the decomposition of extract and sugar, alcohol production, pH drop-down and flavour components were assembled. *Saccharomyces* yeasts fermented very similar at both chosen temperatures [12 and 18 °C). On the other hand, the *Schizosaccharomyces* yeasts as well as the *Brettanomyces* yeasts were clearly faster with higher temperatures. In respect to the development of flavour components, no uniform pattern could be established, neither regarding the temperature dependence nor to what extent the developed values are comparable to the well-known barley malt beers. Thus, all attempts showed a sum of aliphatic alcohols ranging between 23 and 267 μg/L. The sum of aromatic alcohols ranged between 2437 and 11 844 μg/L. The sum of esters ranged from 188 to 2543 μg/L. Altogether proso millet wort was shown to be a substrate that can be fermented without difficulties, with appropriate pH decrease, appropriate alcohol yield and broad flavour component range. Consequently, it can be concluded that different gluten-free beer types can be produced by means of this wort combined with a suitable yeast selection and yeast technology.

6 Conclusion

Cereals have a long utilization history by humans. Cereals are staple foods, and are an important source of nutrients in, both, developed and developing countries. Cereals and cereal products are also an important source of energy, carbohydrates, proteins and fibres, they furthermore contain a valuable range of micronutrients. Even nowadays, a great interest for cereal beverages and foods continues to arise. This concern is promoted by epidemiological studies, which show that consumption of whole grains and grain-based products is associated with health benefits and reduces the risk of chronic diseases. Minor cereals, pseudocereals and other alternative crops produced in small amounts over the previous centuries are now being reintroduced in Europe for the production of functional foods [132]. Many of these cereals and pseudocereals are quite suitable for the production of malt and beer. More specifically gluten free cereals were the focus of recent research, for the production of fermented beverages for celiac disease sufferers [144]. Proso millet (*Panicum miliaceum* L.) may be regarded as one of these minor cereals, which has a high potential as an alternative food ingredient especially in regions, where the growing conditions for cereals like wheat, barley among others are not sufficient.

The percentage and composition of proso millet starch can be compared to that of major cereals. However, the starch properties differ and must be considered when developing production processes such as malting. The gelatinization temperature is important for the wort production. All analysed samples had a gelatinization temperature above 67 °C and had to be separately mashed in a sort of adjunct mashing process. In contrast to the starch content, proso millet contains much higher amounts of dietary fibre than most common cereals. However, the processing method has a major influence on the residual dietary fiber amount in processed foods. The amount of resistant starch in native and, even more, in processed proso millet starch makes it an attractive ingredient for healthy foods and beverage elaboration. Since the analysed proso millet varieties did not show high viscosity values, this fraction can be so far neglected with respect to difficulties in the technical process. The protein composition of proso millet shows reasonable in vitro digestibility. Studies in which rats were monitored under a proso millet protein rich diet showed that the cereal helps prevent liver injuries; moreover, it impacts favourably the cholesterol metabolism. Like other grains proso millet may contribute to the significant supply of antioxidants to help prevent oxidative stress. Anyhow these components need further investigations in regard to malting and beer production. With regard to lipid composition, proso millet contains a high level of polyunsaturated essential fatty acids. Linoleic acid is the major fatty acid present in proso millet. Making this cereal a good source of carotenoids, niacin and thiamine but again processing impacts the final level. Nevertheless the content can be seen in a good balance, so that sufficient fatty acids were availabe for yeast nutrition and flavour stability was not affected. Proso millet minerals are comparable, both, in amount and composition to the levels of other cereals and are therewith deficient in calcium. With regard to anti-nutrients, trypsin and chymotrypsin inhibitor activities were found. The trypsin inhibitor showed higher activity than the inhibitor of chymotrypsin. In addition to the protease inhibitors, an α-amylase inhibitor specific for human pancreatic amylase was also purified from proso millet seeds.

The potential of proso millet being a major ingredient in the daily diet for e. g. celiac sufferers is still under discussion. Some organisations dealing with the acceptance of grains suitable for celiac sufferers have either accepted proso millet or put it under reserve as gluten-free until more data are available [133]. Furthermore, it is important to remark that proso millet should not be consumed in a crude form since hard silica can irritate the gastric- and intestinal mucosa. Thus, people suffering of celiac disease are not recommended to eat crude millet [134].

Proso millet shows over all components a similarity to common cereals, thus on base of this literature it can be concluded that proso millet can be recommended for malting and brewing.

However, it is important that further research in proso millet is done.

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Appendix

Table 1 Estimated world and regional production (in thousand tons) of different millets in 1981–1985 (official and FAO estimates based on country information, modified by *Marathee* (1994))

	Total (kt)	Pearl millet	Foxtail millet	Proso millet	Finger millet	Teff millet	Fonio	Others
Africa	9.557	7.330	–	–	0.855	1.063[a]	0.309	–
Asia	17.048	6.013	5.462	2.279	2.905	–	–	0.386
World	29.295	13.351	5.489	4.931	3.763	1.063	0.309	0.387
World (%)	100.0	45.6	18.7	16.8	12.8	3.6	1.1	1.3

[a] data obtained only from Ethiopia

Table 2 Means, maximum value and minimum value for crude protein and amino acid composition of different independent measurements. The range of the means include also values of investigations where no minimum and maximum were given. Amino acids in italics are essential, while the remaining amino acids are non-essential

Parameter	Maximum [a, b]	Minimum [a, b]	Means [a, c]
Lysin (Lys)	3.48	1.60	1.24–3.30
Histidin (His)	3.94	2.30	1.31–2.83
Threonin (Thr)	4.50	3.70	3.02–4.08
Valine (Val)	7.30	4.69	4.80–6.40
Methionin (Met)	4.30	3.40	2.22–4.10
Isoleucin (Ile)	5.81	4.22	3.91–5.34
Leucine (Leu)	14.70	12.52	13.00–14.00
Tryptophane (Trp)	n. n.	n. n.	1.33
Phenylalanine (Phe)	6.82	5.62	5.60–6.30
Arginin (Arg)	4.30	4.00	2.75–4.10
Aspartic Acid (Asp)	12.00	6.60	5.77–11.27
Serine (Ser)	7.90	4.43	4.91–7.60
Glutamic Acid (Glu)	25.40	21.94	21.58–25.20
Proline (Pro)	7.90	7.60	7.19–7.80
Cysteine (Cys)	1.10	0.90	1.00–1.69
Glycine (Gly)	4.73	2.80	2.13–4.48
Alanine (Ala)	12.40	9.68	10.27–11.70
Tyrosine (Tyr)	4.70	4.30	3.64–4.50
Protein [d]	16.30	12.12	9.88–14.40

[a] Amino acid data is expressed in grams per 100 g protein

[b] From Ravindran (1992), Kalinova and Moudry (2006)

[c] From Ravindran (1992), Kasaoka et al (1999), Kalinova and Moudry (2006)

[d] Protein content is expressed in % of dry weight

Table 3 **Recommended amino acid by FAO/WHO/UNU.**
Tyrosine and cysteine are non-essential amino acids, but they can spare the requirement for phenylalanine and methionine, respectively

Parameter	Maximum [a]	Children (2–5 years) [a, b]	Amino Acid Score in %
Lysin (Lys)	3.48	5.80	60.00
Histidin (His)	3.94	–	–
Threonin (Thr)	4.50	3.40	132.35
Valine (Val)	7.30	3.50	208.57
Methionin (Met)	4.30	2.50 c)	239.60
Cysteine (Cys)	1.69		
Isoleucin (Ile)	5.81	2.80	207.50
Leucine (Leu)	14.70	6.60	222.73
Tryptophane (Trp)	1.33	1.10	120.91
Phenylalanine (Phe)	6.82	6.30 d)	182.86
Tyrosine (Tyr)	4.70		

[a] Amino acid data is expressed in grams per 100 g protein
[b] From FAO/WHO/UNU (1985)
[c] Methionin + Cysteine
[d] Phenylalanine +Tyrosine

Table 4 **Data for the essential amino acid content of proso. Tyrosine and cysteine are not essential amino acids, but they can spare the requirement for phenylalanine and methionine, respectively**

Parameter	Minimum [a]	Children (2–5 years) [a, b]	Amino Acid Score in %
Lysine (Lys)	1.24	5.80	21.38
Histidin (His)	1.31	–	–
Threonin (Thr)	3.02	3.40	88.82
Valine (Val)	4.69	3.50	134.00
Cysteine (Cys)	0.90	2.50 c)	124.80
Methionin (Met)	2.22		
Isoleucin (Ile)	3.91	2.80	139.64
Leucine (Leu)	12.52	6.60	189.70
Tryptophane (Trp)	1.33	1.10	120.91
Phenylalanine (Phe)	5.60	6.30 d)	146.67
Tyrosine (Tyr)	3.64		

[a] Amino acid data is expressed in grams per 100 g protein
[b] From FAO/WHO/UNU (1985)
[c] Methionin + Cysteine
[d] Phenylalanine +Tyrosine

Table 5 **Constituents and lipid subclasses (% w/w) in proso millet and their corresponding fatty acid composition (% w/w)** [a]

	% of SC [b]	**16:0**	**18:0**	**18:1**	**18:2**	**18:3**
Nonpolar lipid subclasses						
Triacylglycerols	81.2	6.4	1	23.8	64.7	1.8
Diacylglycerols	2.9	36.5	12.1	13.8	33.1	3.8
Monoacylglycerols	1.1	–	–	–	–	–
Free fatty acids	4	11.9	3.2	22	59.9	2.8
Free sterols	7.8	–	–	–	–	–
Steryl esters	3	11.1	2.2	22.2	62.4	1.2
Glycolipid subclasses						
Sterylglycosides	12.5	–	–	–	–	–
Esterified sterylglycosides	29.5	20.5	4.9	13.8	56.6	4
Cerebrosides	2	23.4	7.6	13.3	52.5	3.2
Digalactosyldiglycerides	11.5	26.8	4.5	14.3	49	5.4
Monogalactosyldiglycerides	40.4	12.8	3.4	15.4	63.6	4.8
Monogalactosylmonoglycerides	4.1	23.6	7.2	12.1	53.6	3.5
Phospholipid subclasses						
Phosphatidic acid	1.5	40.2	10.2	12.8	31.5	5.3
Phosphatidylglycerol	Traces	–	–	–	–	–
Phosphatidylethanolamine	30	20.7	4	23.3	47.5	4.5
Phosphatidylcholine	36.8	21.4	3.5	20.6	48.3	6.2
Lysophosphatidylcholine	22	23.8	3.8	17.3	49.4	5.7
Phosphatidylserine	8.5	34.3	5.3	8.6	46.4	5.4
Phosphatidylinositol	Traces	–	–	–	–	–

[a] Figure before colon indicates the number of carbon atoms and the figure after colon the number of double bonds in the fatty acid chain

[b] SC = subclass

Table 6 **Contingents of lipid subclasses (% w/w) in proso millet and their corresponding fatty acid composition (% w/w)** [a]

	% of SC [b]	20:0	20:4	22:0	22:1
Nonpolar lipid subclasses					
Triacylglycerols	81.2	0.8	0.4	0.7	0.4
Diacylglycerols	2.9	–	–	0.7	–
Monoacylglycerols	1.1	–	–	–	–
Free fatty acids	4	–	–	0.2	–
Free sterols	7.8	–	–	–	–
Steryl esters	3	–	0.1	0.2	0.6
Glycolipid subclasses					
Sterylglycosides	12.5	–	–	–	–
Esterified sterylglycosides	29.5	–	–	0.2	–
Cerebrosides	2	–	–	–	–
Digalactosyldiglycerides	11.5	–	–	–	–
Monogalactosyldiglycerides	40.4	–	–	–	–
Monogalactosylmonoglycerides	4.1	–	–	–	–
Phospholipid subclasses					
Phosphatidic acid	1.5	–	–	–	–
Phosphatidylglycerol	traces	–	–	–	–
Phosphatidylethanolamine	30	–	–	–	–
Phosphatidylcholine	36.8	–	–	–	–
Lysophosphatidylcholine	22	–	–	–	–
Phosphatidylserine	8.5	–	–	–	–
Phosphatidylinositol	traces	–	–	–	–

[a] Figure before colon indicates the number of carbon atoms and the figure after colon the number of double bonds in the fatty acid chain

[b] SC = subclass

Table 7 Mineral composition of proso millet [a] and the recommended daily intake

Minerals	mg/100 g sample (dry weight basis)	recommended daily intake (mg) [b]
Ash	1500.00–4200.00	–
Sodium	2.8–60.0	100–550
Potassium	235.0–370.0	400–2000
Calcium	7.3–30.0	220–1200
Magnesium	120.0–145.2	24–400
Phosphorus	230.0–362.6	120–1250
Trace minerals		
Zinc	1.72–11.00	1.0–11.0
Iron	4.20–20.00	0.5–20
Manganese	0.8–19	0.6–5.0
Copper	0.83–4.00	0.2–1.5

[a] From Gabrovská et al. (2002), Ravindran (1992), Serna-Saldivar and Rooney (1995)

[b] Values recommended by Deutsche Gesellschaft für Ernährung (2007) depending on age groups, sex, and physiological condition

Table 8 Vitamin composition of proso millet [a] and the recommended daily intake

vitamins	mg/100 g sample (dry weight basis)	recommended daily intake (mg) [b]
Thiamine	0.56–0.66	0.2–1.4
Niacin	1.82–6.39	2.0–18.0
Riboflavin	0.12–0.22	0.3–1.6
Pantothenic acid	0.68–1.10	2.0–6.0
Carotenoids[c]	1.09	0.1–1.5[d]
Choline[e]	78.93	–
Tocopherols[f]	0.26	3.0–17.0

[a] From Gabrovská et al. (2002), Serna-Saldivar and Rooney (1995), Oelke et al. (1990), Bookwalter et al. (1987)

[b] Values recommended by Deutsche Gesellschaft für Ernährung (2007) depending on age groups, sex, and physiological condition

[c] A part of the carotenoids (e.g. β-carotin) are precursors of vitamin A = provitamin A

[d] Values in retinol-equivalent: 1 mg retinol-equivalent = 6 mg all-trans-β-carotin = 12 mg of other provitamin A-carotenoids

[e] Choline was termed as vitamin B_4 in former times

[f] Values in α-tocopherol equivalent

Table 9 Contents of total phenolic acids in proso millet whole grain grits [a]

Phenolic acids	mg/kg sample (dry weight basis)
caffeic acid	1.2 ± 0.1
ferulic acid	290.0 ± 8.8
vanillic acid	12.3 ± 2.0
p-coumaric acid	20.1 ± 1.4
p-hydroxybenzoic acid	3.4 ± 0.2
syringic acid	2.3 ± 1.1
ferulic acid dehydrodimers	87.2 ± 10.3
Total	417.2

[a] From *Mattila et al.*, [1]

[1] Mattila, P.; Pihlava, J.-M. and Hellstroem, J.: Contents of Phenolic Acids, Alkyl- and Alkenylresorcinols, and Avenanthramides in Commercial Grain Products. In: J. Agric. Food Chem. **53** (2005), pp. 8290-8295.

Fig. 1.1 Seeds of diverse varieties of proso millet (*Panicum miliaceum* L.).

Fig. 1.2 Seeds of diverse varieties of proso millet (*Panicum miliaceum* L.)

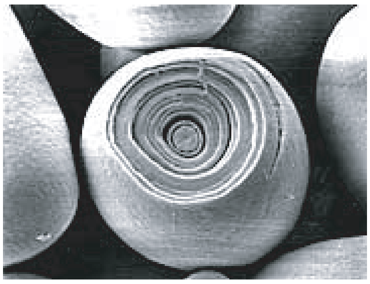


Fig. 2.1 Electron microscopy picture of a truncated starch granule in proso millet (Anonymous, 2007)

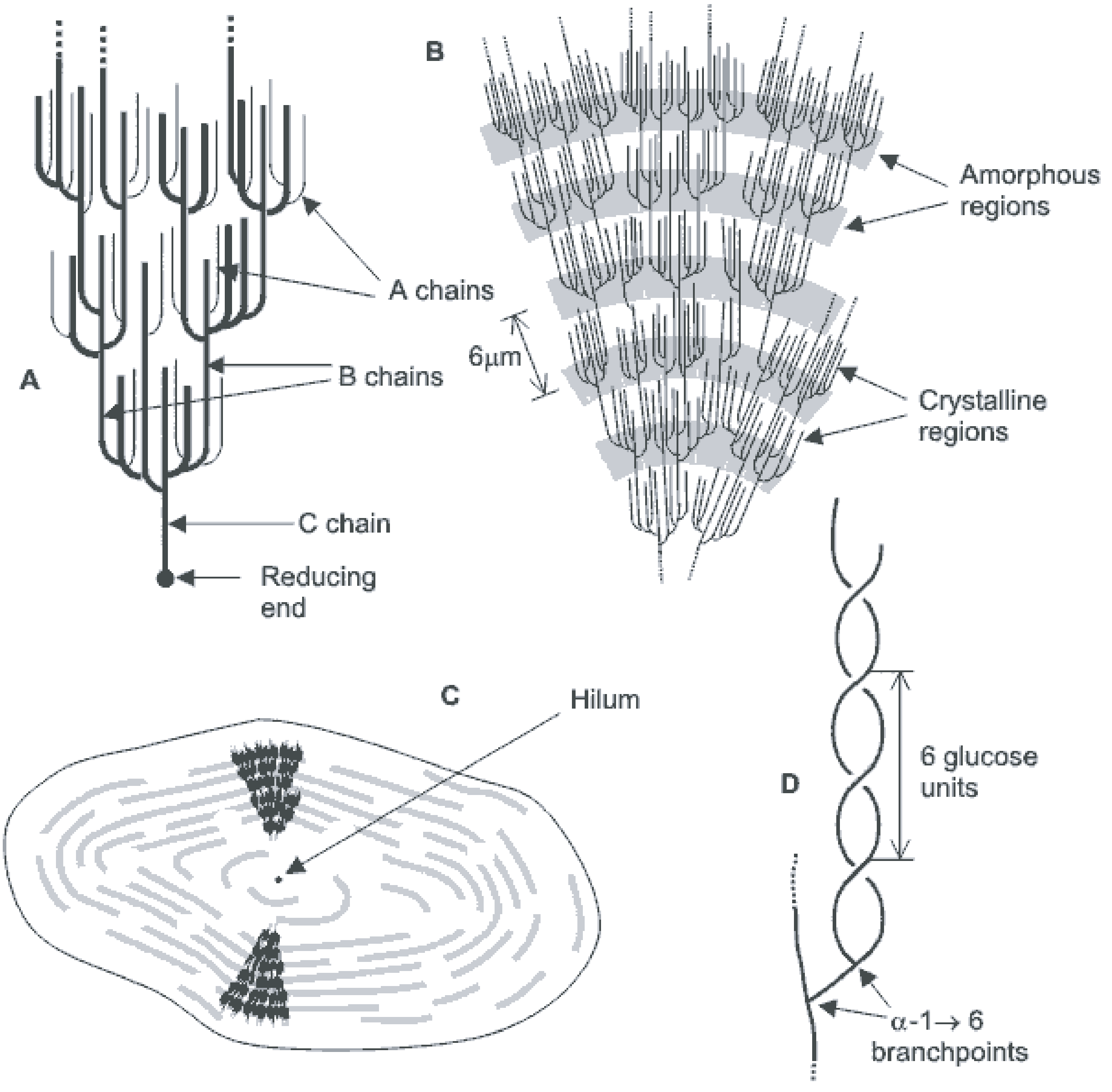
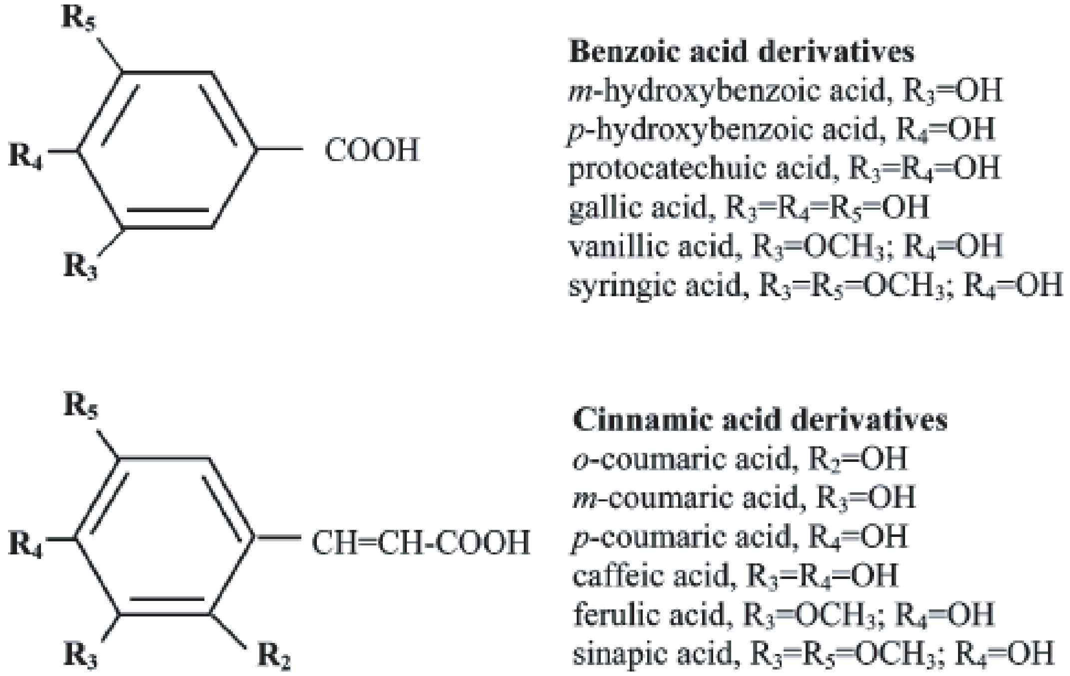


Fig. 2.2 *A*, shows the essential features of amylopectin. *B*, shows the organization of the amorphous and crystalline regions (or domains) of the structure generating the concentric layers that contribute to the "growth rings" that are visible by Scanning Electron Microscopy (SEM). *C*, shows the orientation of the amylopectin molecules in a cross section of an idealized entire granule. *D*, shows the likely double helix structure taken up by neighbouring chains and giving rise to the extensive degree of crystallinity in granule (Chaplin, 2006)



Benzoic acid derivatives
m-hydroxybenzoic acid, R_3=OH
p-hydroxybenzoic acid, R_4=OH
protocatechuic acid, R_3=R_4=OH
gallic acid, R_3=R_4=R_5=OH
vanillic acid, R_3=OCH_3; R_4=OH
syringic acid, R_3=R_5=OCH_3; R_4=OH

Cinnamic acid derivatives
o-coumaric acid, R_2=OH
m-coumaric acid, R_3=OH
p-coumaric acid, R_4=OH
caffeic acid, R_3=R_4=OH
ferulic acid, R_3=OCH_3; R_4=OH
sinapic acid, R_3=R_5=OCH_3; R_4=OH

Fig. 3 Chemical structures of monomeric phenolic acids

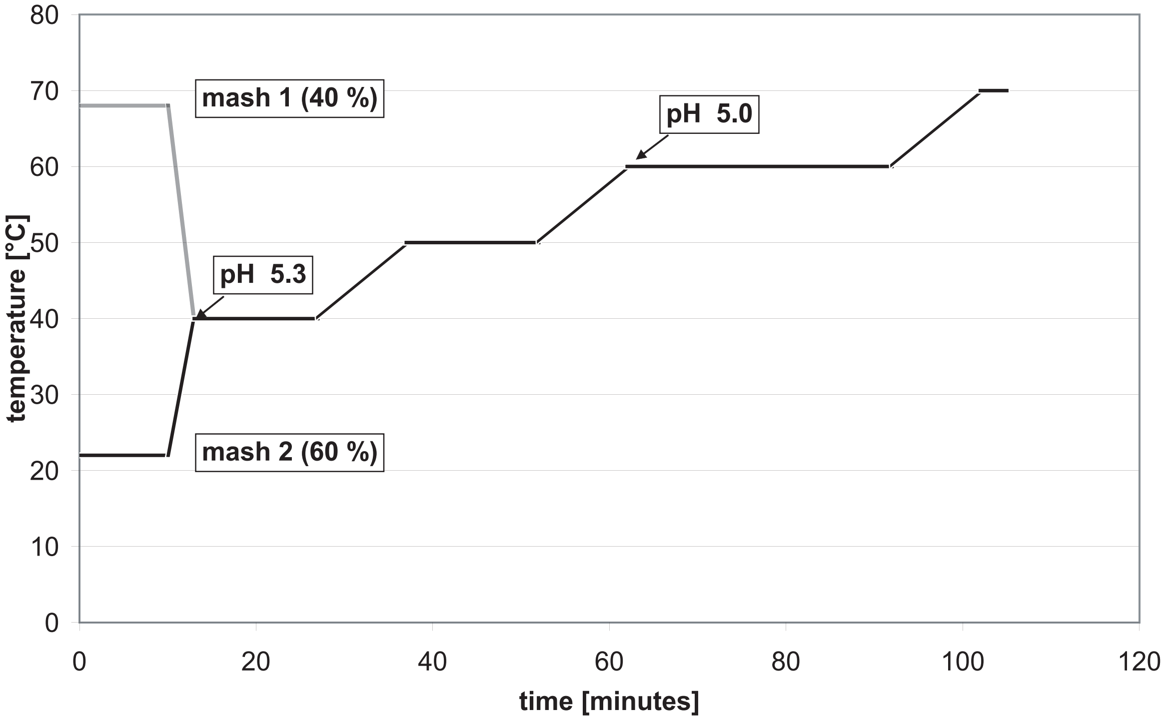


Fig. 4 Optimal mashing program with optimal temperatures and pH adjusting with respect to α-amylase, β-amylase and α-glucosidase of proso millet malt